

学校编码: 10384

密级\_\_\_\_\_

学 号: 33120121151642

厦 门 大 学

硕 士 学 位 论 文

# 九龙江河口沉积物中汞的时空变化研究

Study on temporal and spatial variation of mercury  
in sediments of Jiulongjiang Estuary

高亚芹

指导教师姓名: 袁东星 教授

专 业 名 称: 环 境 科 学

论文提交日期: 2015 年 5 月

论文答辩时间: 2015 年 5 月

2015 年 5 月

## 厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为( )课题(组)的研究成果,获得( )课题(组)经费或实验室的资助,在( )实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

## 厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（        ） 1. 经厦门大学保密委员会审查核定的保密学位论文，  
于        年        月        日解密，解密后适用上述授权。

（        ） 2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年        月        日

# 目 录

摘要.....	I
ABSTRACT.....	III
缩略语表.....	VI
第 1 章 绪论.....	1
1.1 汞的性质及危害.....	1
1.2 汞的来源及循环.....	2
1.3 土壤和沉积物中汞的研究进展.....	5
1.4 汞的同位素及其在污染研究中的应用.....	7
1.5 研究背景和课题的提出.....	10
1.5.1 研究区域概况.....	10
1.5.2 研究背景.....	12
1.5.3 研究目的、研究内容和技术路线.....	14
第 1 章参考文献.....	14
第 2 章 研究方法.....	19
2.1 样品的采集.....	19
2.1.1 柱状沉积物.....	19
2.1.2 表层沉积物.....	21
2.2 样品的分析.....	22
2.2.1 总汞分析.....	22
2.2.1.1 主要仪器与试剂.....	23
2.2.1.2 样品预处理.....	24
2.2.1.3 样品测定.....	24
2.2.2 甲基汞分析.....	26
2.2.2.1 主要仪器与试剂.....	26

2.2.2.2 样品预处理.....	27
2.2.2.3 样品测定.....	28
2.2.3 汞同位素分析.....	29
2.2.3.1 主要仪器与试剂.....	29
2.2.3.2 样品预处理.....	30
2.2.3.3 样品测定.....	30
2.2.4 环境参数的测定.....	30
2.2.4.1 主要仪器与试剂.....	30
2.2.4.2 铅同位素定年.....	31
2.2.4.3 总有机碳测定.....	32
2.2.4.4 硫化物测定.....	32
第2章参考文献.....	33
<b>第 3 章 九龙江红树林区柱状沉积物中汞的污染累积特征.....</b>	<b>34</b>
3.1 引言.....	34
3.2 实验部分.....	34
3.3 结果与讨论.....	34
3.3.1 沉积物的沉积速率.....	34
3.3.2 总汞和甲基汞分布特征.....	36
3.3.2.1 总汞分布特征.....	36
3.3.2.2 甲基汞分布特征.....	38
3.3.2.3 甲基汞占总汞比值.....	39
3.3.3 汞同位素组成和分馏特征.....	40
3.3.4 总汞和甲基汞与总有机碳的相关性分析.....	43
3.4 本章小结.....	46
第3章参考文献.....	47
<b>第4章 九龙江河口表层沉积物中汞的污染特征和来源识别.....</b>	<b>49</b>
4.1 引言.....	49

<b>4.2 实验部分</b>	<b>49</b>
<b>4.3 结果与讨论</b>	<b>50</b>
4.3.1 总汞分布特征	50
4.3.2 总汞与总有机碳及硫化物的相关性分析	52
4.3.3 厦门SY电厂脱硫海水对海域沉积物中汞污染的影响评价	54
4.3.3.1 汞污染特征	54
4.3.3.2 汞污染生态风险评价	55
4.3.4 汞同位素组成和分馏特征	56
4.3.4.1 汞同位素组成特征	56
4.3.4.2 汞污染溯源	59
<b>4.4 本章小结</b>	<b>60</b>
<b>第4章参考文献</b>	<b>61</b>
<b>第5章 总结与展望</b>	<b>63</b>
5.1 研究总结	63
5.2 本研究的不足与展望	64
<b>攻读硕士学位期间发表的论文</b>	<b>65</b>
<b>致谢</b>	<b>66</b>

<b>Table of Contents</b>	
<b>ABSTRACT (in Chinese).....</b>	<b>I</b>
<b>ABSTRACT (in English).....</b>	<b>III</b>
<b>List of Abbreviations.....</b>	<b>VI</b>
<b>Chapter 1 Preface.....</b>	<b>1</b>
<b>1.1 Properties and harmfulness of mercury.....</b>	<b>1</b>
<b>1.2 Sources and cycling of mercury.....</b>	<b>2</b>
<b>1.3 Research progress of mercury in soil and sediment.....</b>	<b>5</b>
<b>1.4 Mercury isotope and its application in pollution study.....</b>	<b>7</b>
<b>1.5 Objectives and contents of this research.....</b>	<b>10</b>
1.5.1 Overview of the research area.....	10
1.5.2 Research background.....	12
1.5.3 Research objectives, contents and approach.....	14
<b>References for Chapter 1 .....</b>	<b>14</b>
<b>Chapter 2 Research methods.....</b>	<b>19</b>
<b>2.1 Sampling.....</b>	<b>19</b>
2.1.1 Core sediment.....	19
2.1.2 Surface sediment.....	21
2.1.3 Research objectives, contents and approach.....	22
<b>2.2 Analyses of samples.....</b>	<b>22</b>
2.2.1 Analyses of total mercury.....	22
2.2.1.1 Instruments and reagents.....	23
2.2.1.2 Sample pretreatment.....	24
2.2.1.3 Sample analysis.....	24
2.2.2 Analyses of methyl mercury.....	26
2.2.2.1 Instruments and reagents.....	26
2.2.2.2 Sample pretreatment.....	27
2.2.2.3 Sample analysis.....	28

2.2.3 Analyses of mercury isotope.....	29
2.2.3.1 Instruments and reagents.....	29
2.2.3.2 Sample pretreatment.....	30
2.2.3.3 Sample analysis.....	30
2.2.4 Analyses of other environmental parameters.....	30
2.2.4.1 Instruments and reagents.....	30
2.2.4.2 Dating with lead isotope .....	31
2.2.4.3 Analyses of total organic carbon.....	32
2.2.4.4 Analyses of sulfid.....	32
<b>References for Chapter 2 .....</b>	<b>33</b>
<b>Chapter 3 Historical record of mercury pollution in core sediments of the mangrove ecosystem at Jiulongjiang Estuary.....</b>	<b>34</b>
<b>3.1 Introduction.....</b>	<b>34</b>
<b>3.2 Experimentation.....</b>	<b>34</b>
<b>3.3 Results and discussion.....</b>	<b>34</b>
3.3.1 Sedimentation rate.....	34
3.3.2 Distribution characteristics of total and methyl mercury.....	36
3.3.2.1 Distribution characteristics of total mercury .....	36
3.3.2.2 Distribution characteristics of methyl mercury .....	38
3.3.2.3 Ratios of methyl mercury to total mercury .....	39
3.3.3 Composition and fractionation characteristics of total mercury isotope .....	40
3.3.4 Relationships of total mercury, methyl mercury and total organic carbon .....	43
<b>3.4 Summary of Chapter 3.....</b>	<b>46</b>
<b>References for Chapter 3 .....</b>	<b>47</b>
<b>Chapter 4 Pollution characteristics and source identification of mercury in surface sediments at Jiulongjiang Estuary.....</b>	<b>49</b>



<b>4.1 Introduction.....</b>	<b>49</b>
<b>4.2 Experimentation.....</b>	<b>49</b>
<b>4.3 Results and discussion.....</b>	<b>50</b>
4.3.1 Distribution characteristics of total mercury.....	50
4.3.2 Relationships of total mercury, total organic carbon and sulfide.....	52
4.3.3 Assessment of the influence of desulfurized seawater discharged from SY power plant on mercury pollution in sediments.....	54
4.3.3.1 Characteristics of mercury pollution.....	54
4.3.3.2 Ecological risk assessment of mercury pollution.....	55
4.3.4 Composition and fractionation characteristics of total mercury isotope .....	56
4.3.4.1 Composition and characteristics of total mercury isotope.....	56
4.3.4.2 Tracing of mercury pollution.....	59
<b>4.4 Summary of Chapter 4.....</b>	<b>60</b>
<b>References for Chapter 4 .....</b>	<b>61</b>
<b>Chapter 5 Contribution and perspectives.....</b>	<b>63</b>
<b>5.1 Summary of research.....</b>	<b>63</b>
<b>5.2 Shortages and perspectives.....</b>	<b>64</b>
<b>Published articles.....</b>	<b>65</b>
<b>Acknowledgements.....</b>	<b>66</b>

## 摘 要

汞是一种可全球循环的持久性有毒污染物。在全球对汞污染状况越来越重视的大背景下,作为福建省第二大河流以及厦漳地区主要水源地的九龙江的汞污染理应受到更多关注。厦门 SY 电厂是九龙江河口区域内汞污染的重要点源,对其周边海域沉积环境进行长期监测并作综合评价,是十分必要的。常规的汞浓度及形态分析法在汞污染的溯源及追踪方面显得无能为力,而近年来兴起的稳定同位素分析技术,为深入研究汞污染源及迁移转化提供了新方法。

本文以九龙江河口为研究区域,探讨沉积物中汞的污染特征,解析汞的来源,主要内容和结果如下:

(1) 在福建龙海九龙江口红树林省级自然保护区的林内和林外光滩,各采集一根柱状沉积物样;对其中的总汞、甲基汞、汞同位素、总有机碳以及铅定年等参数进行测定,分析污染累积特征。结果显示:光滩柱状样总沉积时间为 32 年,沉积速率转折点发生在 1992 年左右,即该地自 1992 年起水文特征发生较大变化。林内柱状样的沉积受到较大干扰,无法得到准确的定年信息。光滩柱状样的总汞浓度范围为 116.0~435.3 ng/g,均值 190.8 ng/g;甲基汞浓度范围为 0.18~0.52 ng/g,均值 0.26 ng/g;甲基汞占总汞比值的范围为 0.11%~0.20%,均值 0.14%。林内柱状样的总汞浓度范围 71.75~145.5 ng/g,均值 121.3 ng/g;甲基汞浓度范围 0.39~1.03 ng/g,均值 0.58 ng/g;甲基汞占总汞比值的范围为 0.36%~0.71%,均值 0.47%。总体上,林内柱状样的总汞浓度比光滩的低,甲基汞浓度比光滩的高。林内柱状样中甲基汞浓度和甲基汞占总汞比值随采样深度的增加呈现先增后降的趋势。两根柱状样中的汞同位素均发生了明显的负的质量分馏(Mass dependent fractionation, MDF),光滩所受的人为源的影响更大。据分析,光致还原反应是光滩柱状样中汞同位素非质量分馏(Mass independent fractionation, MIF)的主要因素。总汞含量与有机碳含量并无显著相关性,说明总有机碳可能不是研究区域内影响汞甲基化的主要因子。

(2) 在九龙江河口区沿河端向海端采集 10 个站位的表层沉积物样;对其中的总汞、汞同位素、总有机碳以及硫化物进行测定,解析汞的来源。结果显示:

河口区表层沉积物中总汞浓度位于 24.8~140.4 ng/g 范围内, 均值为 100.9 ng/g, 汞污染水平较低。总汞与总有机碳成显著正相关关系, 与硫化物无相关性, 说明总有机碳是研究区域内影响总汞含量的主要因子, 硫化物的影响弱于总有机碳。 $\delta^{202}\text{Hg}$  介于-1.86‰~0.11‰之间, 均值-0.74‰;  $\Delta^{199}\text{Hg}$  介于-0.10‰~0.11‰之间, 均值 0.03‰;  $\Delta^{201}\text{Hg}$  介于-0.01‰~0.54‰之间, 均值 0.34‰。沉积物中存在负的汞同位素 MDF 和正的奇数汞同位素 MIF, 光致还原反应对表层沉积物中汞同位素 MIF 的贡献率较大。表层沉积物及悬浮颗粒物的汞同位素组成特征不尽相同, 说明沉积物中汞 MDF 特征并不能完全反映其同站位颗粒物的汞 MDF。汞的二元混合模型的应用结果说明 SY 电厂并非本研究区域唯一的汞污染人为源。九龙江河口区的汞污染很可能来自多个点源甚至是面源。

(3) 根据本课题组自2008年冬季至今对厦门SY电厂脱硫海水排放海域的长期监测数据, 综合分析该海域表层沉积物中汞污染, 评价SY电厂脱硫海水对海域沉积物中汞含量的影响。结果显示: SY电厂脱硫海水排放海域各长期监测站位的总汞浓度无明显的季节变化, 排水口的总汞浓度略高于参考点。监测站位汞的生态危害系数很高, 大部分具有很强的生态危害, 该海域环境的潜在生态危害不容小觑。

**关键词:** 各形态汞; 汞同位素; 九龙江河口; 柱状沉积物; 表层沉积物

**ABSTRACT**

Mercury (Hg) is a persistent global cycle toxic pollutant. More and more attention has been paid to the global Hg pollution. Jiulongjiang River is the second largest river in Fujian Province, as well as the major drinking water source of Xiamen and Zhangzhou. Hg pollution in Jiulongjiang River deserves more concerns. Xiamen SY power plant is an important point source of Hg pollution at Jiulongjiang Estuary, thus long term monitoring and comprehensive evaluation of the sedimentary environment in its adjacent sea area is necessary. The traditional methods of concentration and speciation of Hg cannot meet the requirement of Hg sources tracking. However, technique of stable isotope analysis opens a way out. It provides a new method for further study of source, migration and transformation of Hg.

In this study, the Jiulongjiang Estuary was chosen as the study area to explore the pollution characteristics and analyze the sources of Hg in sediments. The main contents and results are as follows:

(1) A study was carried out to investigate the characteristics of cumulative pollution in core sediments collected from inside and outside of a mangrove forest located in Longhai, Jiulongjiang Estuary. Total mercury (THg), methyl mercury (MeHg), Hg isotopes, total organic carbon (TOC) and  $^{210}\text{Pb}_{\text{ex}}$  were determined. Total deposition time of bare flat (G) core was 32 years. The turning point of deposition rate occurred at about 1992, suggesting that the hydrological characteristics of the site had a change at 1992. Mangrove (H) core suffered obvious interference during the deposition process, showing no accurate dating information. In core G, concentrations of THg were in a range of 116.0~435.3 ng/g, with an average of 190.8 ng/g; MeHg ranged in 0.18~0.52 ng/g, with an average of 0.26 ng/g; the ratio of MeHg/THg was between 0.11%~0.20%, and average was 0.14%. In core H, concentrations of THg were between 71.75~145.5 ng/g, with an average of 121.3 ng/g; MeHg 0.36~1.03 ng/g, average 0.58 ng/g; the ratio of MeHg/THg 0.36%~0.71%, average 0.47%. Overall, THg concentration of core H was lower than that of G, while MeHg concentration of core H was higher than that of G. The concentrations of THg and the

ratio of MeHg/THg in core H firstly increased and then decreased as the sampling depth increased. Obviously negative mass dependent fractionation (MDF) and significant mass independent fractionation (MIF) of odd Hg isotope were observed in both cores. Core G suffered a greater impact of anthropogenic sources. The Hg MIF of G was mainly due to photoreduction reaction. Correlation analysis found that in the cores the THg and MeHg concentration had no significant correlation with TOC, indicating that TOC might not be the main factor impacting Hg methylation in the study region.

(2) THg, Hg isotopes, TOC and sulfide had been determined in surface sediments collected from 10 stations at Jiulongjiang Estuary for analyses of sources of Hg. The concentrations of THg were in a range of 24.8~140.4 ng/g, with an average of 100.9 ng/g, showing low level of Hg contamination. Correlation analysis found that the THg concentration had significant positive correlation with TOC but no correlation with sulfide. The data meant that TOC could be the main factor impacting THg concentration in the study region, and the impact of sulfide was weaker than TOC. The value of  $\delta^{202}\text{Hg}$  ranged in -1.86‰~0.11‰, with an average of -0.74‰; and  $\Delta^{199}\text{Hg}$  was in -0.10‰~0.11‰, average 0.03‰; and  $\Delta^{201}\text{Hg}$  in -0.01‰~0.54‰, average 0.34‰. The isotope analysis results showed that negative MDF and positive MIF of odd Hg isotope existed in the sediments. Photoreduction reaction was the main reason of the Hg MIF. The difference of Hg isotope compositions between surface sediments and suspended particles indicated that the MDF of Hg in sediment was not equal to that in the suspended particles collected from the same station. The application of Hg binary mixture model presented a result that SY power plant was not the only anthropogenic source of Hg pollution in the study area. Hg pollution in Jiulongjiang Estuary is likely to derive from multiple point sources and even surface sources.

(3) Based on the long term monitoring data of the sea area near the discharging outlet of the desulfurized seawater from SY power plant since winter 2008, a comprehensive analysis of Hg pollution in surface sediments was carried out to assess the impact of Hg concentration in desulfurization seawater on the nearby sea

sediments. The THg concentration of both two monitoring stations had no significant seasonal variation. THg concentration at the discharging outlet was slightly higher than that at a reference point. High ecological risk index were ranked for the long term monitoring stations, and most of them showed a strong ecological hazard. Potential ecological harm to the marine environment should not be underestimated.

**Keywords:** Various forms of mercury; Mercury isotopes; Jiulongjing Estuary; Core sediment; Surface sediment

## 缩略语表

CFCVG	Continuous flow cold vapor generation	连续流冷蒸气发生
EPA	Environmental Protection Agency	环境保护署
MC-ICP-MS	Multi-collector inductively coupled plasma mass spectrometer	多接收器电感耦合 等离子体质谱仪
MDF	Mass dependent fractionation	质量分馏
MeHg	Methyl mercury	甲基汞
MIE	Magnetic isotope effect	磁同位素效应
MIF	Mass independent fractionation	非质量分馏
NVE	Nuclear volume effect	核体积效应
PFA	Polyfluoroalkoxy	可溶性聚四氟乙烯
THg	Total mercury	总汞
TOC	Total organic carbon	总有机碳
UNEP	United Nations Environment Programme	联合国环境规划署
WHO	World Health Organization	世界卫生组织

## 第1章 绪论

### 1.1 汞的性质及危害

汞，相对原子量 200.59，位于元素周期表第六周期、第ⅡB族。汞是地壳中相当稀少的一种元素，丰度约为 7 ng/g<sup>[1]</sup>，自然界中罕见于金属单质，常见于朱砂、氯硫汞矿、硫汞锑矿和其他矿物，其中以朱砂最为常见。汞是在常温、常压下呈液态的唯一重金属，易流动，易挥发，且温度越高挥发量越大。汞的化学性质较稳定，不能从酸溶液中置换出氢，但容易与除铁以外的大部分普通金属形成合金，这些汞合金统称汞齐<sup>[2]</sup>。其中金汞齐常用于炼金，钠汞齐常用作有机合成中的还原剂，也被用于高压钠灯中。汞在自然界中的主要存在形式包括元素态汞、二价态汞和有机汞。

汞是高毒性物质，已被世界卫生组织（World Health Organization, WHO）、联合国环境规划署（United Nations Environment Programme, UNEP）和美国环境保护署（Environmental Protection Agency, EPA）等机构列为优先控制污染物。多种汞化合物被列入我国《剧毒物品品名表》，如氯化汞、砷化汞、氧化汞等<sup>[3]</sup>。汞可在各种生态系统中进行生物累积和生物放大，通过皮肤、呼吸道、消化道进入人体，对人体健康和环境生态安全产生重大威胁。除职业接触外，被汞污染的食物、空气、护肤品以及牙科汞合金是人体暴露于汞的主要途径。

不同形态汞的毒性差异较大。无机汞不具有脂溶性，容易排出体外，毒性相对较小。微量的氯化亚汞还可用作口服泻剂。有机汞的毒性较大，其中又以甲基汞（Methyl mercury, MeHg）的毒性最大。MeHg 易被生物吸收蓄积，富集倍数高达  $10^6 \sim 10^7$ ，对人体主要表现为神经毒性和致畸作用<sup>[4]</sup>。汞中毒以慢性毒性为主，症状表现为神经衰弱综合征、汞毒性震颤、口腔炎和肝肾损伤等。低剂量长时间的 MeHg 暴露会损害神经系统。急性毒性通常表现为呕吐、气喘、心脏衰弱等症状，严重时会导致昏厥甚至死亡<sup>[5]</sup>。MeHg 易与生物大分子中的巯基结合，随血液循环系统扩散至全身，并能轻易透过血-脑屏障在脑组织中蓄积，干扰氨基酸的生化功能，造成脑部神经系统的直接损害，对孕妇、婴幼儿等脆弱群体的



Degree papers are in the “[Xiamen University Electronic Theses and Dissertations Database](#)”.

Fulltexts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to [etd@xmu.edu.cn](mailto:etd@xmu.edu.cn) for delivery details.